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Synthesis, Structures, and Catalytic Properties of Constrained Geometry Cyclopentadienyl-phenoxytitanium Dichlorides

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The synthesis of four new bidentate ligands, 2-(3,4-diphenylcyclopentadienyl)-6-phenylphenol ((DCPP)H_2, **7**), 2-(3,4-diphenylcyclopentadienyl)-6-*tert*-butylphenol ((DCBP)H_2, **8**), 2-(3,4-diphenylcyclopentadienyl)-4, 6-di-*tert*-butylphenol (DCDBP)H_2, **9**), and 2-(3,4-diphenylcyclopentadienyl)-6-methylphenol ((DCMP)H_2, **10**), as well as their corresponding constrained geometry cyclopentadienyl-phenoxytitanium dichlorides ((DCPP)$TiCl_2$ (**11**), (DCBP)$TiCl_2$ (**12**), (DCDBP)$TiCl_2$ (**13**), and (DCMP)$TiCl_2$ (**14**)), are described. Complexes **11**−**14** were synthesized from the reaction of $TiCl_4$ with the corresponding dilithio salt of the ligand. Molecular structures of **11** and **12** were determined by single-crystal X-ray diffraction studies. The Cp(cent)−Ti−O angles of 107.4° for **11** and 106.7° for **12** reveal their sterically open features as catalyst precursors. When activated with $^{i}Bu_3Al$ and $Ph_3C^+B(C_6F_5)_4^-$, complexes **11**−**14** exhibit reasonable catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melt transition temperatures. Compounds **12** and **13** show good catalytic activity for copolymerization of ethylene with 1-hexene.

Introduction

Group 4 constrained geometry metallocene catalysts have received extensive attention in recent years because of their importance in industrial applications.[1] In particular the constrained geometry catalysts with a pendent nitrogen[2] donor on the cyclopentadienyl ligand, such as $Me_2Si(\eta^5\text{-}Me_4C_5)(^tBuN)MX_2$ (**1**, M = Ti, Zr, Hf; X = Cl, Me, CH_2Ph),[3] have been widely studied in industry as well as academic institutions.[4] On the other hand, a considerable number of catalysts with a pendent oxygen[5] donor on the cyclopentadienyl ligand have also been reported. Among them, the tetramethylcyclopentadienyl-4-methylphenoxytitanium dibenzyl complex, (TCP)$Ti(CH_2Ph)_2$ (**2**), is particularly interesting due to its structural features and good catalytic activities.[6] However, the synthesis of this type of catalyst was found to be difficult. Marks et al. have tried various synthetic strategies, and only the dibenzyl titanium complex **2** was obtained. Since then, there have been no further reports on the synthesis and catalytic properties of this

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(1) (a) Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickas, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. Eur. Pat. Appl. EP 416 815 A2, 1991 (Dow). (b) Canich, J. A. M. Eur. Pat. Appl. EP 420436-Al, 1991, (Exxon). (c) Canich, J. A. M.; Hlatky, G. G.; Turner, H. W. PCT Appl. WO 92-00333, 1992. (d) Canich, J. A. M. U.S. Patent 5,026,798, 1991 (Exxon). (e) Canich, J. A. M. Licciard, G. F. U.S. Patent 5,057,475, 1991 (Exxon).

(2) McKnight, A. L., Waymouth, R. M. *Chem. Rev.* **1998**, *96*, 2587−2598.

(3) (a) Hughes, A. K.; Meetsma, A.; Teuben, J. H. *Organometallics* **1993**, *12*, 1936−1945. (b) du Plooy, K. E.; Moll, U.; Wocadol, S.; Massa, W.; Okuda, J. *Organometallics* **1995**, *14*, 3129−3131. (c) Okuda, J.; Verch, S.; Spaniol, T. P.; Stuermer, R. *Chem. Ber.* **1996**, *129*, 1429−1431. (d) Canich, J. M. PCT Int. Appl. WO 96/00244, 1996 (Exxon). (e) Amor, F.; Okuda, J. *J. Organomet. Chem.* **1996**, *520*, 245−248. (f) Okuda, J.; Eberle, T.; Spaniol, T. P. *Chem. Ber.* **1997**. *130*, 209−215. (g) Park, J. T.; Yoon, S. C.; Bae, B.-J.; Seo, W. S.; Suh, I.-H.; Han, T. K.; Park, J. R. *Organometallics* **2000**, *19*, 1269−1276. (h) Dahlmann, M.; Schottek, J.; Fröhlich, R.; Kunz, D.; Nissinen, M.; Erker, G.; Fink, G.; Kleinschmidt, R. *J. Chem. Soc., Dalton Trans.* **2000**, 1881−1886.

(4) (a) Bunnel, E. E.; Burger, B. J.; Bercaw, J. E. *J. Am. Chem. Soc.* **1988**, *110*, 976−978. (b) Piers, W. E.; Shapiro, P. J.; Bunel, E. E.; Bercaw, J. E. *Synlett* **1990**, *2*, 74−84. (c) Shapiro, P. J.; Bunel, E. E.; Schaefer, W. P.; Bercaw, J. E. *Organometallics* **1990**, *9*, 867−869. (d) Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **1994**, *116*, 4623−4640. (e) Okuda, J. *Chem. Ber.* **1990**, *123*, 1649−1651. (f) Chen, Y. X.; Stern, C. L.; Yang, S.; Marks, T. J. *J. Am. Chem. Soc.* **1996**, *118*, 12451−12452. (g) Alt, H. G.; Reb, A.; Milins, W.; Weis, A. *J. Organomet. Chem.* **2001**, *628*, 169−182.

(5) (a) Siemeling, U. *Chem. Rev.* **2000**, *100*, 1495−1526. (b) Rau, A.; Schmitz, S.; Luft, G. *J. Organomet. Chem.* **2000**, *608*, 71−75. (c) Christie, S. D. R.; Man, K. W.; Whitby, R. J.; Slawin, A. M. Z. *Organometallics* **1999**, *18*, 348−359. (d) Gielens, E. E. C. G.; Tiesnitsch, J. Y.; Hessen, B.; Teuben, J. H. *Organometallics* **1998**, *17*, 1652−1654. (e) van der Zeijden, A. A. H.; Matteis, C. *Organometallics* **1997**, *16*, 2651−2658. (f) Trouve, G.; Laske, D. A.; Meetsma, A.; Teuben, J. H. *J. Organomet. Chem.* **1996**, *511*, 255−262. (g) Christoffers, J.; Bergman, R. G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2266−2267. (h) Huang, Q.; Qian, Y.; Li, G.; Tang, Y. *Transition Met. Chem.* **1990**, *15*, 483−485. (i) Kunz, K.; Erker, G.; Kehr, G.; Fröhlich, R.; Jacobsen, H.; Berke, H.; Blacque, O. *J. Am. Chem. Soc.* **2002**, *124*, 3316−3324. (j) Qian, Y. L.; Huang, J. L. *Polyhedron* **1994**, *13*, 1105−1108.

(6) Chen, Y. X., Marks, T. J. *Organometallics* **1997**, *16*, 5958−5963.

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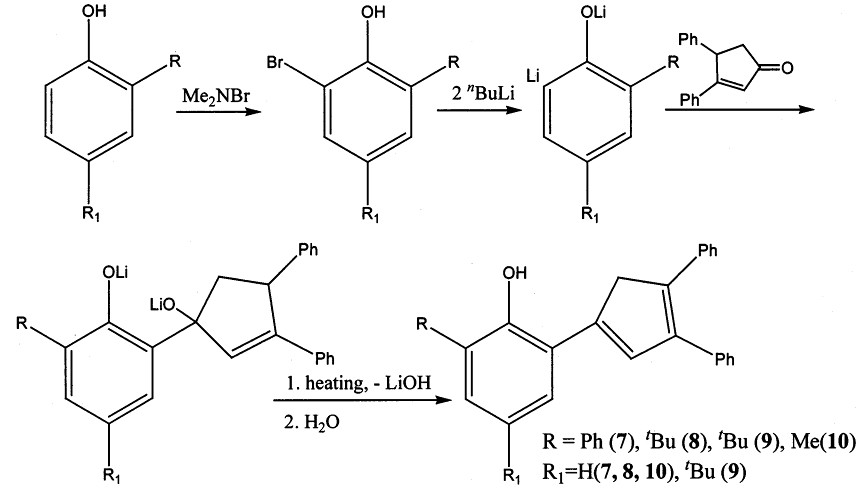
Scheme 1. Synthetic Procedure of Ligands 7−10



type of catalyst until a very recent communication.[7] We have recently modified the ligand by introducing sterically bulky substituents to the cyclopentadienyl and phenoxy groups in order to prevent the formation of multinuclear species and biscyclopentadienyl complexes. With the modified ligands, a number of new Cp-phenoxy titanium(IV) dichloride complexes have been synthesized for the first time. We report here the convenient preparation of 2-(3,4-diphenylcyclopentadienyl)-6-phenylphenol ((DCPP)H_2, **7**), 2-(3,4-diphenylcyclopentadienyl)-6-*tert*-butylphenol ((DCBP)H_2, **8**), 2-(3,4-diphenylcyclopentadienyl)-4,6-di-*tert*-butylphenol ((DCDBP)H_2, **9**), and 2-(3,4-diphenylcyclopentadienyl)-6-methylphenol ((DCMP)H_2, **10**), and the synthesis and characterization of the corresponding titanium(IV) dichloride complexes ((DCPP)$TiCl_2$, **11**), ((DCBP)$TiCl_2$, **12**), ((DCDBP)$TiCl_2$, **13**), and ((DCMP)$TiCl_2$, **14**), as well as their catalytic performance in ethylene polymerization and copolymerization with 1-hexene.

Results and Discussion

Design and Synthesis of Ligands. Besides the above-mentioned reason, the ligands were designed also with following considerations: (1) The bulky substituent at the *ortho* position of the phenol and the two phenyl groups on the Cp ring construct a relatively crowded environment around the Ti metal center, thus could prevent the complex from dimerization through Cl and O atoms, and coordination through the O atom to the Al atom in methylaluminoxane (MAO) or trialkylaluminum. (2) The two electron-withdrawing Ph groups on the Cp ring of the ligands would reduce the electron density of the Cp^- and its reactivity in the metalation reaction, therefore increasing the selectivity of forming the desired complexes in their synthetic reactions. The ligands **7**−**10** were synthesized by a modified literature procedure.[6,8] The reaction of the dilithio salt of the corresponding 2-bromophenol, which was obtained by treating 2-bromo-6-phenylphenol (**3**), 2-bromo-6-*tert*-butylphenol (**4**), 2-bromo-4,6-di-*tert*-butylphenol (**5**), or 2-bromo-6-methylphenol (**6**) with ^{n}BuLi, with 3,4-diphenyl-2-cyclopentenone in toluene at room temperature followed by heating the reaction mixture at 65 °C produces **7**−**10** respectively (Scheme 1). We have tried the reaction in different solvents and found that reactions carried out in Et_2O or THF gave no desired product. In addition, **7**−**10** were obtained in higher yields through the lithium hydroxide elimination route by heating the reaction mixture directly. Reactions carried out in a normal way with the dehydration step with concentrated HCl give products in low yields. Compounds **7**−**10** were found to be stable under inert atmosphere. Decomposition occurred when they were left in air for several hours with a gradual color change from pale yellow to dark brown. The 2-bromophenols **3**−**6** were prepared from the reaction of Me_2NBr with the corresponding phenol in toluene at −15 °C. It is necessary to keep the reaction at lower temperatures in order to increase the selectivity and reduce the multibromination byproducts. Compound **5** was obtained in highest yield among **3**−**6** due to the existence of the *tert*-butyl group at the *para* position of the starting phenol. Compounds **3**−**10** were characterized by elemental analysis and NMR spectroscopy.

Synthesis of Titanium(IV) Dichloride Complexes 11−14. Attempts to prepare the titanium(IV) dichloride complexes through amine elimination,[3a,9] alkane elimination,[6,10] or Me_3SiCl elimination[11] approaches were unsuccessful. Complexes **11**−**14** were finally synthesized in moderate yields by the traditional reaction of $TiCl_4$ with the dilithio salt of the corresponding ligand **7**−**10** in toluene (Scheme 2). Considering the fact that **2** could not be synthesized by lithium salt

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[7] Turner, L. E., Thorn, M. G., Fanwick, P. E., Pothwell, I. P. *Chem. Commun.* **2003**, 1034−1035.

[8] (a) Zhang, F.; Mu, Y.; Zhao, L. G..; Zhang, Y. T.; Bu, W. M.; Chen, C. X.; Zhai, H. M.; Han, H.; *J. Organomet. Chem.* **2000**, *613*, 68−76. (b) Zhang, F.; Mu, Y.; Wang, J. H.; Shi, Z.; Bu, W. M.; Zhang, Y. T.; Feng, S. H. *Polyhedron* **2000**, *19*, 1941−1947.

[9] (a) Diamond, G. M.; Rodewald, S.; Jordan, R. F. *Organometallics* **1995**, *14*, 5−7. (b) Diamond, G. M.; Jordan, R. F.; Petersen, J. L. *J. Am. Chem. Soc.* **1996**, *118*, 8024−8033. (c) Mu, Y.; Piers, W. E.; MacDonald, M. A.; Zaworotko, M. J. *Can. J. Chem.* **1995**, *73*, 2233−2238. (d) Mu, Y.; Piers, W. E.; MacGillivray, L. R.; Zaworotko, M. J. *Polyhedron* **1995**, *14*, 1−10. (e) Baker, R. W.; Wallace, B. J. *Chem. Commun.* **1999**, 1405−1406.

[10] (a) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J.; Young, V. G., Jr. *Organometallics* **1996**, *15*, 2720−2726. (b) Mu, Y.; Piers, W. E.; MacQuarrie, D. C.; Zaworotko, M. J. *Can. J. Chem.* **1996**, *74*, 1696−1703. (c) Chen, Y. X.; Marks, T. J. *Organometallics* **1997**, *16*, 3649−3657.

[11] (a) Ready, T. E.; Chien, J. C. W.; Rausch, M. D. *J. Organomet. Chem.* **1996**, *519*, 21−28. (b) Cardoso, A. M.; Clark, R. J. H.; Moorhouse, S. *J. Chem. Soc., Dalton Trans.* **1980**, 1156−1160. (c) Winter, C. H.; Zhou, X.-X.; Dobbs, D. A.; Heeg, M. J. *Organometallics* **1991**, *10*, 210−214.

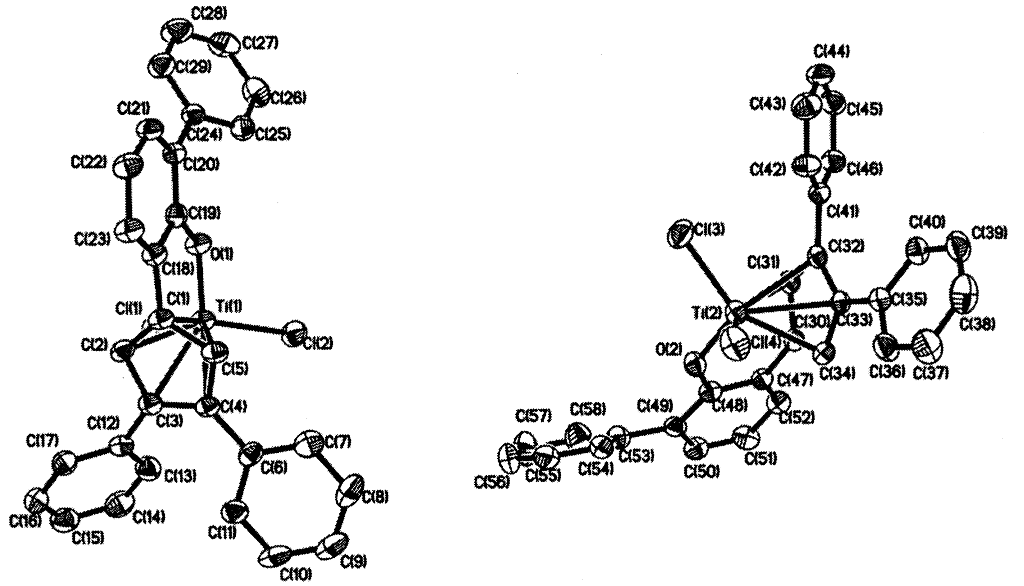
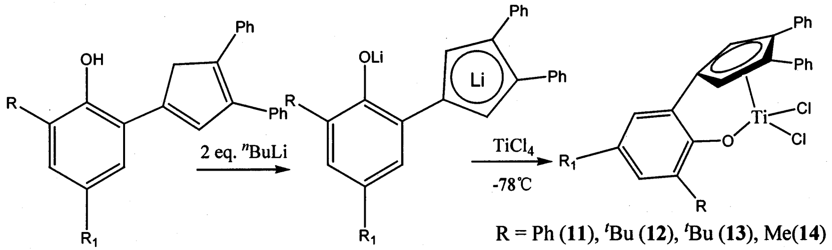


Figure 1. Structure of complex **11** (thermal ellipsoids are drawn at the 30% probability level).

Scheme 2. Synthetic Procedure of Complexes 11–14



R = Ph (**11**), ^{t}Bu (**12**), ^{t}Bu (**13**), Me(**14**)
R_1=H(**11, 12, 14**), ^{t}Bu (**13**)

elimination reaction,[6] the successful synthesis of **11**–**14** indicates that our original consideration of the ligand design is reasonable. The R group at the *ortho* position of the phenolate and the two Ph groups on the Cp ring indeed keep the monoligated titanium(IV) dichloride complex from further reaction with the dilithio salt of the ligand. The yield of the synthetic reaction could be quite different depending on the nature of the R group. The smallest methyl group results in the lowest yield of **14** among these complexes, while the bulky ^{t}Bu group leads to higher yields of **12** and **13**. The complexes **11**–**14** were found to be considerably stable to air and moisture and could be exposed to air for several days without obvious decomposition. These complexes also exhibit good thermostability. They could be heated to 200 °C without decomposition. The ^{1}H and ^{13}C NMR spectra of **11**–**14** indicate that they all have C_s-symmetric structures in solution, and the two Ph groups on the Cp ring are equivalent due to their free rotation at room temperature.

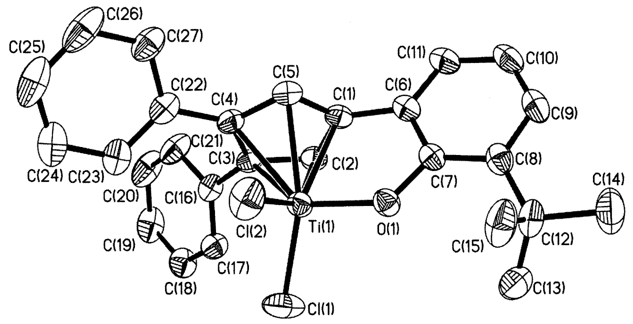


Figure 2. Structure of complex **12** (thermal ellipsoids are drawn at the 30% probability level).

Crystal Structures of 11 and 12. The molecular structures of complexes **11** and **12** were determined by X-ray crystal structure analyses. The ORTEP drawings of the molecular structures are shown in Figure 1 and Figure 2, respectively. The selected bond lengths and angles are summarized in Table 1. There are two independent molecules (**11A** and **11B**) with minor structural differences and a diethyl ether molecule in the unit cell of **11**. Selected bond lengths and angles for **11A** will be used in subsequent discussions. The general structural features of **11** and **12** are comparable to those previously reported for **2**. The geometry around titamium in **11** or **12** can be described as pseudo-tetrahedral with Cp(cent)–Ti–O angles of 107.4° for **11A** and 106.7° for **12**, which are slightly smaller than the one in **2** (107.7°)[6] and the Cp(cent)–Ti–N angle in **1** (107.6°),[1a] indicating sterically open features for **11** and **12** similar to complexes **1** and **2** as catalyst precursors. Both molecules adopt C_s-symmetric structures. The Ti–C_{ring} (av) distances of 2.365 Å for **11A** and 2.362 Å for **12** are identical to that in **2** (2.36(1) Å) and slightly longer than that in **1** (2.340 Å). The distances of Ti–C3 and Ti–C4 in both **11A** and **12** are obviously longer than those of the Ti–C_{ring} bonds, and the Ti–Cp(cent)–C1 angles of **11A** (86.6°) and **12** (86.9°) are less than 90°, which is characteristic for constrained geometry metallocene catalysts.[1,3–6] The phenolate plane–Ph_2Cp plane dihedral angle is 89.7° for **11A** and 86.5° for **12**, and the

Table 1. Selected Bond Lengths and Angles

	Complex **11A**		
Ti(1)–O(1)	1.813(4)	Ti(1)–C(1)	2.302(6)
Ti(1)–C(2)	2.323(6)	Ti(1)–C(3)	2.409(6)
Ti(1)–C(4)	2.456(6)	Ti(1)–C(5)	2.335(6)
Ti(1)–Cl(1)	2.255(2)	Ti(1)–Cl(2)	2.237(2)
O(1)–C(19)	1.397(7)	Cp (cent)–Ti(1)	2.031
C(1)–C(18)	1.495(8)	C(3)–C(12)	1.484(9)
C(4)–C(6)	1.465(8)	O(1)–Ti(1)–Cl(1)	103.88(15)
O(1)–Ti(1)–Cl(2)	104.15(15)	Cl(1)–Ti(1)–Cl(2)	105.58(8)
Cp1(cent)–Ti(1)–O(1)	107.4	Ti(1)–Cp1(cent)–C(1)	86.6
C(18)–C(1)–Cp(cent)	169.9	C(1)–C(18)–C(19)	112.9(5)
C(18)–C(19)–O(1)	114.1(5)	C(19)–O(1)–Ti(1)	129.1(4)
	Complex **11B**		
Ti(2)–O(2)	1.821(4)	Ti(2)–C(31)	2.325(6)
Ti(2)–C(32)	2.404(6)	Ti(2)–C(33)	2.442(6)
Ti(2)–C(34)	2.336(6)	Ti(2)–C(30)	2.309(6)
Ti(2)–Cl(3)	2.249(2)	Ti(2)–Cl(4)	2.242(2)
O(2)–C(48)	1.388(7)	Cp2(cent)–Ti(2)	2.033
C(30)–C(47)	1.490(8)	C(32)–C(41)	1.495(8)
C(33)–C(35)	1.465(8)	O(2)–Ti(2)–Cl(3)	103.72(16)
O(2)–Ti(2)–Cl(4)	105.47(15)	Cl(3)–Ti(2)–Cl(4)	104.66(9)
Cp2(cent)–Ti(2)–O(2)	107.3	Ti(2)–Cp2(cent)–C(30)	86.9
C(47)–C(30)–Cp2(cent)	169.2	C(30)–C(47)–C(48)	113.4(5)
C(47)–C(48)–O(2)	114.9(6)	C(48)–O(2)–Ti(2)	128.3(4)
	Complex **12**		
Ti(1)–O(1)	1.818(4)	Ti(1)–C(1)	2.311(6)
Ti(1)–C(2)	2.315(7)	Ti(1)–C(3)	2.440(7)
Ti(1)–C(4)	2.423(6)	Ti(1)–C(5)	2.320(6)
Ti(1)–Cl(1)	2.228(2)	Ti(1)–Cl(2)	2.247(2)
O(1)–C(7)	1.369(6)	Cp (cent)–Ti(1)	2.032
C(1)–C(6)	1.481(9)	C(3)–C(16)	1.489(10)
C(4)–C(22)	1.482(8)	O(1)–Ti(1)–Cl(1)	103.56(14)
O(1)–Ti(1)–Cl(2)	103.60(17)	Cl(1)–Ti(1)–Cl(2)	103.93(10)
Cp(cent)–Ti(1)–O(1)	106.7	Ti(1)–Cp(cent)–C(1)	86.9
C(6)–C(1)–Cp(cent)	169.6	C(1)–C(6)–C(7)	112.7(5)
C(6)–C(7)–O(1)	114.0(5)	C(7)–O(1)–Ti(1)	129.8(4)

(phenolate)C–C(ring) vector in both **11A** and **12** is bent 9.4° from the Cp ring plane. The corresponding data for **2** are 81(1)° and 15(1)°, reflecting less steric strain in **11** and **12** than in **2**. The Ti–O bond lengths of 1.813(4) Å in **11A** and 1.818(4) Å in **12** are shorter than that in **2** (1.851(7) Å), and the Ti–O–C angles of 129.1(4)° in **11A** and 129.8(4)° in **12** are larger than that in **2** (126.6(6)°), indicating more Ti–O double-bond character in **11** and **12**.[4f,12]

Ethylene Polymerization Studies. Complexes **11**–**14** were studied as ethylene polymerization catalysts, and the results are summarized in Table 2. Upon activation with $Al(^iBu)_3$ and $Ph_3C^+B(C_6F_5)_4^-$, complexes **11**–**14** all show good catalytic activity for ethylene polymerization, producing polyethylenes with moderate molecular weights and melt transition temperatures. The order of the catalytic activity for ethylene polymerization under similar conditions (see runs 2, 7, 12, and 15 in Table 2) is **13** > **12** > **11** ≈ **14**, which could obviously be attributed to the nature of the substituents on the phenolate. By examining the structure of these catalysts, it can be clearly seen that the electronic effect of the R_1 group at the *para* position of the phenolate plays a significant role in the catalytic activity when the R group at the *ortho* position is kept the same (comparing **12** and **13**), while both steric and electronic effects of the R group at the *ortho* position seem to be important in determining the order of the catalytic activity when the R_1 group at the *para* position is unchanged (comparing **11**, **12**, and **14**).[13] For all complexes, the catalytic activity increases with the increase in Al/Ti ratio and reaches the highest catalytic activities with the Al/Ti ratio of 40. Further increasing the Al/Ti ratio results in a decrease in the catalytic activity. It is

Table 2. Summary of Ethylene Polymerization Catalyzed by Complexes 11–14 (activated by $Ph_3C^+[B(C_6F_5)_4]^-$)[a]

no.	catalyst	Al:Ti	T (°C)	yield (g)	activity[b]	$M\eta^c \times 10^{-4}$	T_m (°C)[d]
1	**11**	20	80	0.43	433	11	127.4
2	**11**	40	80	0.54	544	20	132.6
3	**11**	60	80	0.32	322	18	130.7
4	**11**	40	100	0.15	151	13	128.1
5	**11**	40	60	0.31	312	14	127.1
6	**12**	20	80	1.43	1380	4.5	122.3
7	**12**	40	80	1.98	1910	4.3	125.4
8	**12**	60	80	1.31	1270	8.9	127.4
9	**12**	40	100	0.92	889	7.1	124.2
10	**12**	40	60	1.09	1050	4.4	124.3
11	**13**	20	80	2.25	2430	2.9	121.7
12	**13**	40	80	3.17	3420	3.8	123.2
13	**13**	60	80	1.91	2060	4.2	121.1
14	**14**	20	80	0.46	406	10	120.9
15	**14**	40	80	0.58	512	9.2	122.5
16	**14**	60	80	0.39	344	9.7	122.1

[a] Polymerization conditions: solvent 50 mL of toluene, catalyst 1 mg, B/Ti ratio 1.5, time 30 min, ethylene pressure 5 bar. [b] kg PE (mol Ti)$^{-1}$ h^{-1}. [c] Measured in decahydronaphthalene at 135 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}.

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(12) (a) Huffman, J. C.; Moloy, K. G.; Marsella, J. A.; Caulton, K. G. *J. Am. Chem. Soc.* **1980**, *102*, 3009–3014. (b) Cetinkaya, B.; Hitchcock, P. B.; Lappert, M. F.; Torroni, S.; Atwood, J. L.; Hunter, W. E.; Zaworotko, M. J. *J. Organomet. Chem.* **1980**, *188*, C31–C 35. (c) Fandos, R.; Meetsma, A.; Teuben, J. H. *Organometallics* **1991**, *10*, 59–60.

(13) Möhring, P. C.; Coville, N. J. *J. Organomet. Chem.* **1994**, *479*, 1–29.

Table 3. Copolymerization of Ethylene with 1-Hexene Catalyzed by Complexes 12 and 13 (activated by $Ph_3C^+B(C_6F_5)_4^-$)[a]

run no.	catalyst	1-hexene (mol/L)	yield (g)	activity[b]	$M\eta^c \times 10^{-3}$	T_m (°C)[d]	1-hexene content[e]
1	**12**	0.40	3.11	3010	5.2	41.4	0.152
2	**12**	0.24	3.78	3650	6.1	76.1	0.130
3	**12**	0.16	2.42	2340	5.9	76.1	0.098
4	**12**	0.08	2.09	2020	13.0	94.9	0.058
5	**13**	0.40	3.85	4150	4.1	40.8	0.151
6	**13**	0.24	4.60	4960	5.5	86.2	0.090
7	**13**	0.16	3.32	3580	7.6	91.6	0.075
8	**13**	0.08	2.87	3090	9.0	104.5	0.051

[a] Polymerization conditions: solvent 50 mL of toluene, temperature 80 °C, catalyst 1 mg, B/Ti ratio 1.5, Al/Ti ratio 40, time 30 min, ethylene pressure 5 bar. [b] kg polymer (mol Ti)$^{-1}$ h^{-1}. [c] Measured in xylene at 105 °C. [d] Determined by DSC at a heating rate of 10 °C min^{-1}. [e] Calculated by ^{13}C NMR spectra.

possible that excessive Al(^{i}Bu)$_3$ would consume so much $Ph_3C^+B(C_6F_5)_4^-$ that the catalyst could not be efficiently activated.[14] The catalytic activity of all complexes is low at room temperature and increases at elevated temperatures, which reflects the nature of tight interaction between the catalyst cation and the cocatalyst anion in the constrained geometry catalyst systems.[10c] It is also worth noting that the lower activity catalysts **11** and **14** give higher viscosity-average molecular weights. One possible explanation for this result is that both the chain propagation and chain termination steps are slow with these catalysts. The slow propagation will ensure having sufficient monomer to coordinate to the catalyst metal center and thus further suppress the chain termination through β-H elimination. ^{13}C NMR analysis of typical polymer samples reveals that the polyethylenes contain mainly ethyl branches together with a small amount of long-chain branches.[15] The degree of ethyl branching is 2−4 branches per 1000 C atoms for samples obtained with **11**, **12**, and **13** and 4−6 branches per 1000 C atoms for samples obtained with **14**. The difference in degree of branching might be responsible for the different melt transitions for samples obtained with **11** and **14**.

Copolymerization of Ethylene with 1-Hexene. Complexes **12** and **13** were also briefly tested for copolymerization of ethylene and 1-hexene, and the results were summarized in Table 3. By comparison with the ethylene homopolymerization results listed in Table 2, a positive comonomer effect on the catalytic activity under our conditions can be obviously seen for the copolymerization systems. ^{13}C NMR analysis[16] of copolymers indicates pretty good incorporation of 1-hexene into the polymer chain for both catalyst systems, although the feed concentration of 1-hexene is quite low for all experiments. Detailed investigations on the copolymerization and the extension of the catalyst family are currently underway.

Conclusions

The constrained geometry cyclopentadienyl-phenoxytitanium dichlorides **11**−**14** can be synthesized with modified ligands **7**−**10** from the reaction of the dilithio salt of the corresponding ligand with $TiCl_4$. Compounds **11**−**14** are considerably stable to air and moisture and can be exposed to air for several days without obvious decomposition. They also have good thermostability and can be heated to 200 °C without decomposition. ^{1}H and ^{13}C NMR spectra and X-ray crystallography indicate that **11**−**14** have C_s-symmetric structures. The Cp(cent)−Ti−O angle is about 107° for these complexes, which is characteristic of constrained geometry metallocene catalysts. Upon activation with Al(^{i}Bu)$_3$ and $Ph_3C^+B(C_6F_5)_4^-$, **11**−**14** exhibit reasonable catalytic activity for ethylene polymerization. The catalytic activity of **11**−**14** is obviously relative to the nature of the substituents at the phenoxy group, and the order of the catalytic activity under similar conditions is **13** > **12** > **11** ≈ **14**. Compounds **12** and **13** show good catalytic activity for copolymerization of ethylene with 1-hexene.

Experimental Section

General Comments. Reactions with organometallic reagents were carried out under a nitrogen atmosphere (ultrahigh purity) using standard Schlenk techniques.[17] Solvents were dried and distilled prior to use.[18] Polymerization grade ethylene was further purified by passage through columns of 10 Å molecular sieves and MnO. Al(^{i}Bu)$_3$, ^{n}BuLi, and $TiCl_4$ were purchased from Aldrich. 3,4-Diphenyl-2-cyclopentenone[19] and $Ph_3C^+B(C_6F_5)_4^-$ [20] were prepared according to literature procedures. NMR spectra were measured using a Varian Unity-400 or Varian Mercury-300 NMR spectrometer. ^{13}C NMR spectra for polymers were recorded at 130 °C. The pulse delay was 8 s. The acquisition time was 1 s. The pulse angle was 90°. The polymer solutions were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt %).

Preparation of 2-Bromo-6-phenylphenol (3). Br_2 (5.9 mL, 0.115 mol) was added dropwise to a solution of Me_2NH (0.12 mol) and NaOH (0.23 mol) in 50 mL of H_2O at −15 °C. The mixture was stirred for 30 min at this temperature and extracted with toluene (100 mL). The organic layer was separated and dried with $MgSO_4$ to give a yellow solution of Me_2NBr, which was added to a solution of 2-phenylphenol (16.5 g, 0.097mol) in 100 mL of toluene at −15 °C. The mixture was stirred for 4 h, slowly warmed to room temperature, and stirred overnight, then acidified with 20 mL of HCl (6 M). The organic layer was separated and dried with $MgSO_4$. Pure product (16.9 g, 70.0%) was obtained by column chromatography over silica (hexanes/CH_2Cl_2, 2:1) as pale purple needles. Anal. Calcd for $C_{12}H_9BrO$ (249.10): C, 57.86; H, 3.64. Found: C, 57.83; H, 3.66. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.369−7.600 (m, 6H, Ph), 7.240 (d, 1H, Ph), 6. 871 (t, 1H, Ph), 5.680 (s, 1H, OH).

Preparation of 2-Bromo-6-*tert*-butylphenol (4). Compound **4** was prepared in the same manner as **3** with 2-*tert*-butylphenol (20 mL, 0.13 mol) as starting material. Pure product (23.9 g, 80.1%) was obtained by distillation under reduced pressure at 89−90 °C/10 mmHg as light yellow oils. Anal. Calcd for $C_{10}H_{13}BrO$ (229.11): C, 52.42; H, 5.72. Found: C, 52.39; H, 5.68. ^{1}H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.326 (d, 1H, Ph), 7.210 (d, 1H, Ph), 6.729 (t, 1H, Ph), 5.798 (s, 1H, OH), 1.395 (s, 9H, Ph-^{t}Bu).

Preparation of 2-Bromo-4,6-Di-*tert*-butylphenol (5). Compound **5** was prepared in the same manner as **3** with 2,4-

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[14] Bochmann, M.; Sarsfield, M. J. *Organometallics* **1998**, *17*, 5908−5912.

[15] Kooko, E.; Lehmus, P.; Leino, R.; Luttikhedde, H. J. G.; ekholm, P. Näsman, J. H.; Seppälä, J. V. *Macromolecules* **2000**, *33*, 9200−9204.

[16] Hsieh, E. T.; Randall, J. C. *Macromolecules* **1982**, *15*, 1402−1406.

[17] Shriver, D. F. *The Manipulation of Air-Sensitive Compounds*; McGraw-Hill: New York, 1969.

[18] Perrin, D. D.; Armarego, W. L. F.; Perrin, D. R. *The Purification of Laboratory Chemicals*; Pergamon: New York, 1980.

[19] Geissmann, T. A.; Koelsch, C. F. *J. Org. Chem.* **1939**, *3*, 489−502.

di-*tert*-butylphenol (22 g, 0.107mol) as starting material. Pure product (25.9 g, 85.2%) was obtained by column chromatography over silica (hexanes) as yellow crystals. Anal. Calcd for $C_{14}H_{21}BrO$ (285.22): C, 58.95; H, 7.42. Found: C, 58.97; H, 7.39. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.316 (s, 1H, Ph), 7.236 (s, 1H, Ph), 5.651 (s, 1H, OH), 1.397 (s, 9H, Ph-^{t}Bu), 1.280 (s, 9H, Ph-^{t}Bu).

Preparation of 2-Bromo-6-methylphenol (6). Compound **6** was prepared in the same manner as **3** with 2-methylphenol (18 g, 0.166 mol) as starting material. Pure product (23.9 g, 76.8%) was obtained by distillation under reduced pressure at 82−83 °C/10 mmHg as brown oils. Anal. Calcd for C_7H_7BrO (187.03): C, 44.95; H, 3.77. Found: C, 44.91; H, 3.80. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.277 (d, 1H, Ph), 7.048 (d, 1H, Ph), 6.693 (t, 1H, Ph), 5.557 (s, 1H, OH), 2.285 (s, 3H, Ph-Me).

Preparation of 2-(3,4-Diphenylcyclopentadienyl)-6-phenylphenol (7). A solution of 2-bromo-6-phenylphenol (3.0 g, 12.0 mmol) in Et_2O (40 mL) was added dropwise to a solution of ^{n}BuLi (25 mmol) in Et_2O (20 mL) at −15 °C. The mixture was slowly warmed to room temperature and stirred overnight. The solvent was removed in vacuo, and the residue was dissolved in toluene (60 mL). The solution was cooled to −15 °C, and a solution of 3,4-diphenyl-2-cyclopentenone (2.8 g, 12.0 mmol) in toluene (40 mL) was added dropwise over an hour. The reaction mixture was stirred overnight and then heated for another 4 h at 65 °C and quenched with 20 mL of saturated NH_4Cl(aq). The organic layer was separated, dried over $MgSO_4$, filtered, and concentrated by distillation under reduced pressure. Pure product (1.8 g, 38.8%) was obtained by column chromatography over silica (hexanes/CH_2Cl_2, 1:2) as yellow needles. Anal. Calcd for $C_{29}H_{22}O$ (386.47): C, 90.12; H, 5.74. Found: C, 90.08; H, 5.71. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.979−7.519 (m, 19H, Cp, Ph), 5.775 (s, 1H, OH), 4.072 (s, 2H, Cp). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 149.761, 142.088, 141.607, 139.169, 137.177, 136.910, 136.807, 135.769, 129.382, 129.317, 128.905, 128.646, 128.420, 128.230, 128.088, 127.791, 127.516, 127.039, 126.444, 123.124, 120.552, 47.230 ppm.

Preparation of 2-(3,4-Diphenylcyclopentadienyl)-6-*tert*-butylphenol (8). Compound **8** was prepared in the same manner as **7** with 2-bromo-6-*tert*-butylphenol (4.35 g, 19 mmol) as starting material. Pure product (3.4 g, 48.8%) was obtained as pale yellow crystals. Anal. Calcd for $C_{27}H_{26}O$ (366.48): C, 88.48; H, 7.15. Found: C, 88.40; H, 7.18. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.894−7.379 (m, 13H, Ph), 6.990 (s, 1H, Cp), 6.056 (s, 1H, OH), 3.941 (s, 2H, Cp), 1.447 (s, 9H, Ph-^{t}Bu). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 151.521, 142.390, 141.249, 140.218, 136.586, 136.395, 136.338, 134.148, 128.562, 128.390, 128.363, 127.844, 127.337, 126.814, 126.406, 126.146, 123.605, 119.850, 48.585, 34.894, 29.617 ppm.

Preparation of 2-(3,4-Diphenylcyclopentadienyl)-4,6-di-*tert*-butylphenol (9). Compound **9** was prepared in the same manner as **7** with 2-bromo-4,6-di-*tert*-butylphenol (4.28 g, 15 mmol) as starting material. Pure product (3.53 g, 55.7%) was obtained as yellow crystals. Anal. Calcd for $C_{31}H_{34}O$ (422.60): C, 88.10; H,8.11. Found: C, 88.06; H, 8.13. ^1H NMR ($CDCl_3$, 400 MHz; 298 K): δ 7.159-7.394 (m, 12H, Ph), 6.961 (s, 1H, Cp), 5.909 (s, 1H, OH), 3.957 (s, 2H, Cp), 1.453 (s, 9H, Ph-^{t}Bu), 1.333 (s, 9H, Ph-^{t}Bu). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 149.124, 142.939, 141.924, 141.203, 140.108, 136.601, 136.456, 135.499, 134.102, 128.543, 128.386, 128.344, 127.860, 127.291, 126.761, 123.483, 123.021, 122.834, 48.661, 35.119, 34.322, 31.598, 29.682 ppm.

Preparation of 2-(3,4-Diphenylcyclopentadienyl)-6-methylphenol (10). Compound **10** was prepared in the same manner as **7** with 2-bromo-6-methylphenol (3.42 g, 18.3 mmol) as starting material. Pure product (2.09 g, 35.2%) was obtained as yellow crystals. Anal. Calcd for $C_{24}H_{20}O$ (324.41): C, 88.85; H, 6.21. Found: C, 88.80; H, 6.18. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 6.841−7.409 (m, 14H, Ph, Cp), 5.529 (s, 1H, OH), 3.978 (s, 2H, Cp), 2.309 (s, 3H, Ph-Me). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 151.364, 142.409, 141.848, 139.917, 137.089, 136.830, 134.560, 129.935, 128.760, 128.645, 128.588, 128.550, 128.069, 127.474, 126.902, 126.295, 124.440, 120.529, 48.054, 16.388 ppm.

Preparation of [η^5;η^1-(3,4-$Ph_2C_5H_2$)-6-phenyl-C_6H_3O]-$TiCl_2$(11). A solution of ^{n}BuLi (5.2 mmol) was added dropwise to a solution of 2-(3,4-diphenylcyclopentadienyl)-6-phenylphenol (1.0 g, 2.6 mmol) in Et_2O (100 mL) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Solvent was removed in vacuo, and the residue was washed with hexane and then dissolved in toluene (150 mL). A solution of $TiCl_4$ (2.6 mmol) in toluene (50 mL) was slowly added at −78 °C, and the reaction mixture was stirred at room temperature overnight. The precipitate was filtered off, and the solvent was removed to leave a red solid. Recrystallization from CH_2Cl_2/hexane (1:3) gave pure **11** as red crystals (0.56 g, 39.9%), mp 146−148 °C. Anal. Calcd for $C_{29}H_{20}Cl_2OTi\cdot 0.5C_4H_{10}O$ (540.34): C, 68.91; H, 4.66. Found: C, 67.80; H, 4.59. ^1H NMR (300 MHz, $CDCl_3$, 298 K): δ 7.214 (s, 2H, Cp), 7.164−7.929 (m, 18H, Ph), 3.478 (q, 2H, CH_2 of Et_2O), 1.208 (t, 3H, CH_3 of Et_2O). ^{13}C NMR (75.4 MHz, $CDCl_3$, 298 K): δ 171.629, 144.793, 136.090, 133.548, 132.320, 131.362, 130.439, 130.274, 129.702, 129.301, 129.000, 128.462, 128.336, 127.584, 127.134, 126.260, 124.528, 65.870, 15.282 ppm.

Preparation of [η^5;η^1-(3,4-$Ph_2C_5H_2$)-6-*tert*-butyl-C_6H_3O]-$TiCl_2$ (12). Reaction of the dilithio salt of **8** (2.0 mmol) with $TiCl_4$ (2.0 mmol) in toluene (80 mL) was carried out in the same way as described above for the synthesis of **11**. Pure **12** (0.46 g, 47.6%) was obtained as red crystals, mp 128−130 °C. Anal. Calcd for $C_{27}H_{24}Cl_2OTi$ (483.25): C, 67.11; H, 5.01. Found: C, 67.05; H, 4.96. ^1H NMR ($CDCl_3$, 400 MHz; 298 K): δ 7.165 (s, 2H, Cp), 7.107−7.581 (m, 13H, Ph), 1.366 (s, 9H, Ph-^{t}Bu). ^{13}C NMR ($CDCl_3$, 100.5 MHz; 298 K): δ 173.748, 145.163, 135.786, 133.366, 132.478, 131.469, 130.445, 129.725, 129.209, 128.321, 126.956, 126.000, 124.050, 34.957, 29.624 ppm.

Preparation of [η^5;η^1-(3,4-$Ph_2C_5H_2$)-4,6-di-*tert*-butyl-C_6H_2O]$TiCl_2$ (13). Reaction of the dilithio salt of **9** (1.8 mmol) with $TiCl_4$ (1.8 mmol) in toluene (80 mL) was carried out in the same way as described above for the synthesis of **11**. Pure **13** (0.55 g, 56.6%) was obtained as red crystals, mp 135−137 °C. Anal. Calcd for $C_{31}H_{32}Cl_2OTi$ (539.36): C, 69.03; H, 5.98. Found: C, 68.95; H, 5.94. ^1H NMR ($CDCl_3$, 400 MHz; 298 K): δ 7.330−7.572 (m, 12H, Ph), 7.179 (s, 2H, Cp), 1.366 (s, 18H, Ph-^{t}Bu). ^{13}C NMR ($CDCl_3$, 100.5 MHz; 298 K): δ 171.517, 147.340, 145.512, 134.595, 133.252, 132.622, 131.538, 130.142, 129.732, 129.125, 128.306, 123.807, 122.882, 35.139, 34.881, 31.665, 29.722 ppm.

Preparation of [η^5;η^1-(3,4-$Ph_2C_5H_2$)-6-methyl-C_6H_3O]-$TiCl_2$ (14). Reaction of the dilithio salt of **10** (2.2 mmol) with $TiCl_4$ (2.2 mmol) in toluene (100 mL) was carried out in the same way as described above for the synthesis of **11**. Pure **14** (0.33 g, 34.0%) was obtained as red crystals, mp 207−209 °C. Anal. Calcd for $C_{24}H_{18}Cl_2OTi$ (441.17): C, 65.34; H, 4.11. Found: C, 65.11; H, 4.02. ^1H NMR ($CDCl_3$, 300 MHz; 298 K): δ 7.085−7.568 (m, 13H, Ph), 7.163 (s, 2H, Cp), 2.174 (s, 3H, Ph-Me). ^{13}C NMR ($CDCl_3$, 75.4 MHz; 298 K): δ 173.560, 153.646, 145.614, 133.606, 132.633, 131.763, 129.950, 129.492, 128.565, 128.069, 125.776, 124.269, 123.326, 15.511 ppm.

X-ray Structure Determinations of 11 and 12. Single crystals of **11** and **12** suitable for X-ray structural analysis were obtained from the mixture of CH_2Cl_2/hexane (v/v = 1:3). The data were collected at 293 K on the Siemens P4 four-circle diffractometer for **11** and a Bruker SMART-CCD diffractometer for **12** (graphite-monochromated Mo Kα radiation: λ = 0.71073 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 4. Both

Table 4. Crystal Data and Structural Refinement Details for 11 and 12

	11	**12**
mol formula	$C_{31}H_{25}Cl_2O_{1.5}Ti$	$C_{27}H_{24}Cl_2OTi$
mol wt	540.31	483.26
cryst system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a/Å	11.791(4)	10.458(3)
b/Å	14.111(4)	11.337(3)
c/Å	18.567(6)	13.409(4)
α/deg	78.38(2)	66.697(17)
β/deg	73.45(2)	86.48(2)
γ/deg	66.05(2)	73.363(17)
V/Å^3	2693.4(13)	1396.6(7)
Z	4	2
D_c/g cm^{-3}	1.332	1.149
F(000)	1116	500
abs coeff/mm^{-1}	0.540	0.512
scan type	$\omega-2\theta$	$\omega-2\theta$
collect range, deg	$3.74 \le 2\theta \le 49.98$	$7.04 \le 2\theta \le 46.44$
no. of reflns	11 281	2864
no. of indep reflns	9437	2864
R_{int}	0.0278	0.000
no. of data/restraints/params	9437/7/617	2864/0/280
R	0.0697	0.0733
R_w	0.1953	0.2545
goodness of fit	0.970	1.135
largest diff peak and hole/e Å^{-3}	1.442 −0.312	1.360 −0.308

structures were solved by direct methods[21] and refined by full-matrix least-squares on F^2. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were included in idealized positions. All calculations were performed using the SHELXTL[22] crystallographic software packages.

Polymerization Reactions. A dry 250 mL steel autoclave was charged with 40 mL of toluene, thermostated at the desired temperature, and saturated with ethylene (1.0 bar). The polymerization reaction was started by injection of a mixture of catalyst and $Al(^iBu)_3$ in toluene (5 mL) and a solution of $Ph_3C^+B(C_6F_5)_4^-$ in toluene (5 mL) at the same time. The vessel was repressurized to needed pressure with ethylene immediately, and the pressure was maintained by continuously feeding monomer. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M)/methanol = 1:1]. The mixture was stirred overnight, and the polymer was collected by filtration, washed with water and methanol, and dried in vacuo. For copolymerization experiments, appropriate amounts of 1-hexene were added into the system.

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Note Added after ASAP. This paper was removed from the Web on July 29, 2003, and reinstated on the Web Aug 12, 2003. The order of author names is now changed.

Supporting Information Available: Tables of crystal data and structure refinement, atomic positional parameters, bond lengths and angles, anisotropic temperature factors, and calculated hydrogen atom positions for **11** and **12** and ^1H and ^{13}C NMR spectra for **7**−**14**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[20] (a) Massey, A. G.; Park, A. J. *J. Org. Chem*. **1962**, *2*, 245−250. (b) Massey, A. G.; Park, A. J. *J. Organomet. Chem*. **1966**, *5*, 218−225. (c) Chien, J. C. W.; Tsai, W. M.; Rasch, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 8570−8571.

[21] *SHELXTL*; PC Siemens Analytical X-ray Instruments: Madison WI, 1993.

[22] Sheldrick, G. M. *SHELXTL Structure Determination Programs*, Version 5.0; PC Siemens Analytical Systems: Madison, WI, 1994.